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1,2-Difluorodinitroethylene was prepared by pyrolysis of 1,2-difluorotetra-nitroethane. Reactions of 1,1,-diiododinitroethylene with nucleophiles were studied. Nitrations of 1,1-diamino-2,2-dinitroethylenes gave trinitromethyl derivatives. Fluoride ion reacted with 1,1-diiododinitroethylene to give trifluorodinitroethane salts, used to prepare 3,3,3-trifluoro-2,2-dinitropropyl formal. Thermolysis of 1,1,2-tribromotrinitroethane gave 1,2-and 1,1-dibromodinitroethylene.

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FINAL REPORT

K. Baum

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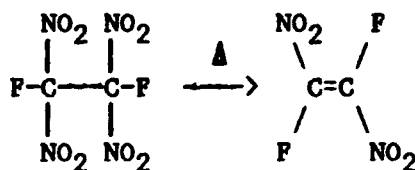
Introduction

This final report summarizes Research on Contract DAAL03-88-C-0013. This work is a continuation of research supported earlier by the Army Research Office under Contracts DAAG29-82-C-0003, DAAG29-79-C-0011 and DAAG29-85-C-0010.

Polynitroolefins are of general theoretical interest for studies of the bonding effects of electronegative organic substituents. They are also of practical interest as building blocks for energetic explosives and propellant ingredients. Under the predecessor ARO contracts, evidence for the formation of tetranitroethylene in solution thermolysis was obtained first by Diels Alder trapping experiments,¹ and subsequently the pure olefin was isolated by flash vacuum pyrolysis.² Pyrolysis of the anthracene adduct of tetranitroethylene gave 11,12-dinitro-9,10-dihydro-9,10-ethenoanthracene,³ the Diels Alder adduct that would be obtained from the unknown dinitroacetylene. Preliminary work on the pyrolysis of 1,2-difluorotetranitroethane indicated that 1,2-difluorodinitroethylene was formed. Also, incomplete work was carried out on the preparation of 1,1-diiododinitroethylene and studies of its reactions with nucleophiles.

Results

On the current contract, work on the preparation and characterization of 1,2-difluorotetranitroethane was completed and published.⁴ The compound was found to be considerably more stable than tetranitroethylene. X-ray diffraction, surprisingly, showed that one of the two nitro groups is out of the plane of the rest of the molecule.

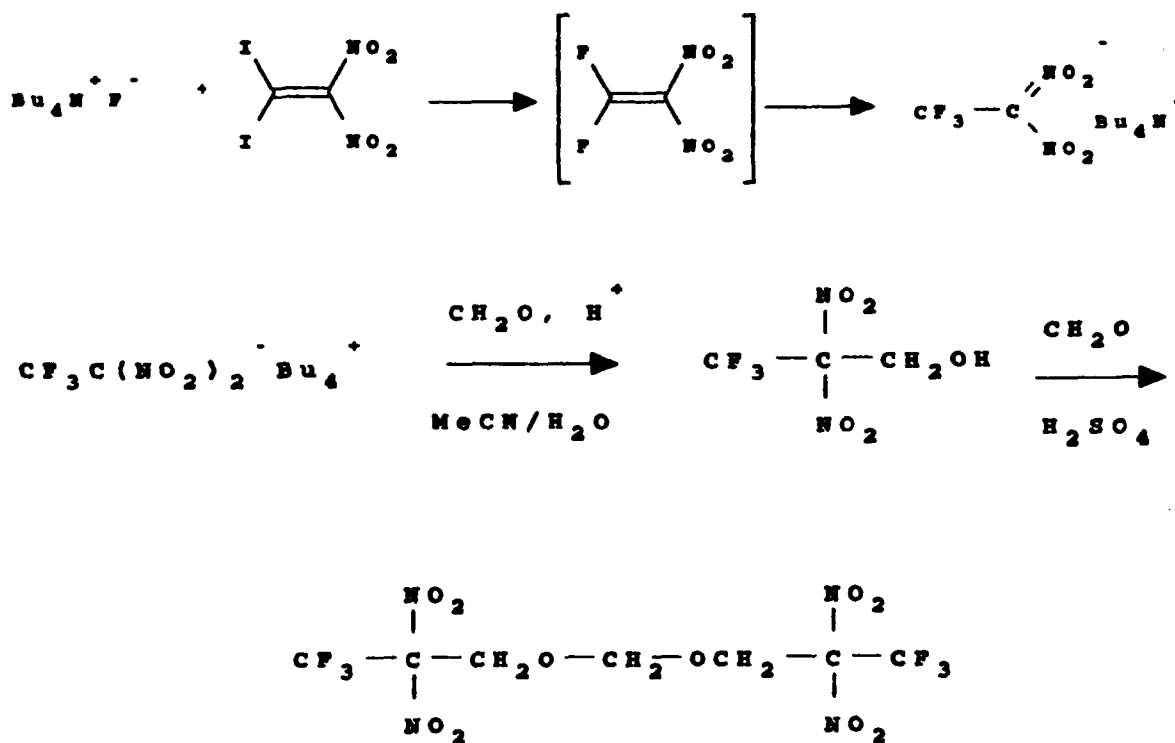


Work initiated on the preceding contract showed that a compound reported in 1900⁵ as 1,2-diiododinitroethylene was actually 1,1-diiododinitroethylene. Additional work on the structure and reactions of this olefin was carried out on the current program, and the work was published.⁶ A noteworthy feature of the structure of 1,1-diiododinitroethylene is that only one nitro group is coplanar with the double bond and the other is twisted out of the plane by 90°. These two examples of geminal and vicinal dinitroolefins exhibiting planarity of only one nitro group with the double bond are unprecedented.

1,1-Diiododinitroethylene underwent facile nucleophilic substitutions and Michael addition reactions.⁶ Simple amines (dimethylamine, propylamine, aniline) gave 1,1-diamino-2,2-dinitroethylene derivatives; diamines (o-phenylenediamine, ethylenediamine, 1,3-diaminopropane, 1,4-diaminobutane) gave the corresponding cyclic products, and a tetramine, tetrakis(aminomethyl)methane gave the analogous spiro derivative. Ammonia gave only ammonium cyanodinitromethide, whereas phenol gave 1,1-dinitro-2,2,2-triphenoxyethane. The reaction of 1,1-Diiododinitroethylene with potassium nitrite gave the dipotassium salt of tetranitroethane. X-ray crystallography of the 1,1-diamino-2,2-dinitroethylenes showed twisting of the double bond, in some cases, with twist angles greater than any previously reported for twisted ethylenes, with concomitant bond distance distortions.

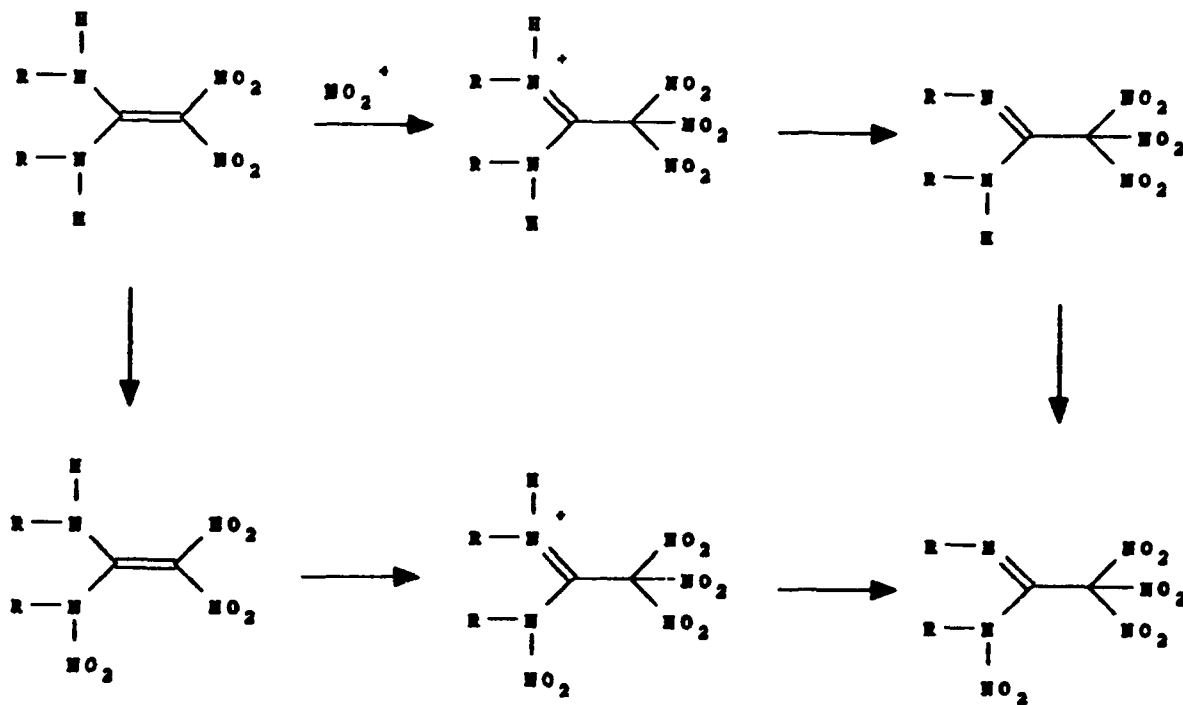
The reaction of 1,1-diiododinitroethylene with fluoride⁷ ion followed a course analogous to that of phenoxide ion. Tetrabutylammonium fluoride gave

the tetrabutylammonium salt of 1,1,1-trifluorodinitroethane, although alkali metal fluorides or lower tetraalkylammonium salts did not give isolable products. The sodium salt of 1,1,1-trifluorodinitroethane could be isolated by metathesis. The reaction of formaldehyde with the tetrabutylammonium salt gave 3,3,3-trifluoro-2,2-dinitropropanol, which was converted to its formal with trioxane and sulfuric acid. This formal is potentially useful as a plasticizer for rocket propellants and explosives because of improved oxidation balance compared to the currently used unfluorinated analog, BDNPF.

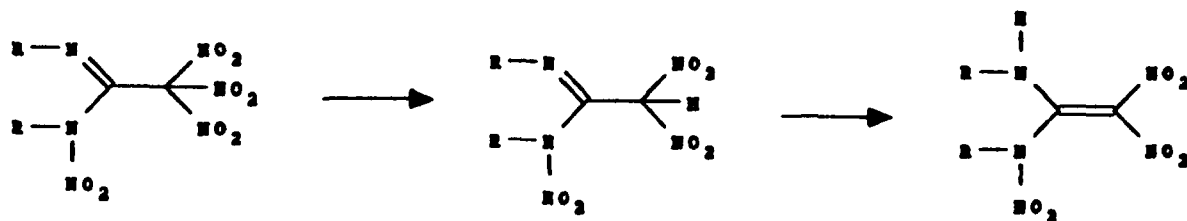


The nitration of 1,1-diamino-2,2-dinitroethylene derivatives, obtained from amines and 1,1-diiododinitroethylene, was studied.¹ Nitrations with nitric acid and trifluoroacetic anhydride gave trinitromethyl nitramino imines in high yield. Formally, the formation of these trinitromethyl derivatives involves

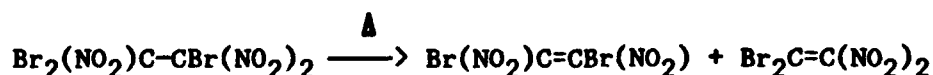
attack of a nitronium ion equivalent on the dinitrovinyl carbon, with loss of a proton on nitrogen, and nitration of the other amine nitrogen. The order of these two steps is unknown.



reductive denitration of the trinitromethyl groups would be expected to give the dinitromethyl analogs, which are tautomeric with N-nitro-1,1-diamino-2,2-dinitro olefins.



Scholl⁷ reported in 1898 that the bromination of the dipotassium salt of tetranitroethane gave 1,1,2-tribromotrinitroethane, which, on heating at 100 °C at 50 mm Hg, gave dibromodinitromethane, tribromonitroethylene, and 1,2-dibromodinitroethylene. The latter compound was identified only by elemental analysis. This report is the only reference in the literature for 1,2-dibromodinitroethylene, and the possible alternative structure, 1,1-dibromodinitroethylene, has not been reported. These reactions were reinvestigated as an extension of our study of polynitroolefins. Both 1,2-dibromodinitroethylene and 1,1-dibromodinitroethylene were obtained by the thermolysis of 1,1,2-tribromotrinitroethane. 1,2-Dibromodinitroethylene reacted with methanol to give methyl bromonitroacetate, and gave a Diels-Alder adduct with cyclopentadiene. 1,1-Dibromodinitroethylene reacted with ethylenediamine to give 2-(dinitromethylene)-1,3-diazacyclopentane, obtained previously from 1,1-diiododinitroethylene.



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"Synthesis and Properties of 1,2-Difluorodinitroethylene", Baum, K.; Archibald, T. G.; Tzeng, D.; Gilardi, R.; Flippen-Anderson, J. L.; George, C., *J. Org. Chem.*, 1991, 56, 537-539.

"Synthesis and Reactions of 1,1-Diododinitroethylene", Baum, K.; Bigelow, S. S.; Nguyen, N. V.; Archibald, T. G.; Gilardi, R.; Flippen-Anderson, J. L.; George, C., *J. Org. Chem.*, 1992, 57, 235-241.

"Nitration of 1,1-Diamino-2,2-dinitroethylenes", Baum, K.; Nguyen, N. V.; Gilardi, R.; Flippen-Anderson, J. L.; George, C., *J. Org. Chem.*, in press.

"Reaction of 1,1-Diododinitroethylene with Fluoride. Preparation of 1,1,1-Trifluorodinitroethane Derivatives", Baum, K.; Bigelow, S. S.; Nguyen, N. V., *Tetrahedron Letters*, in press.

"Preparation of 1,2-Dibromodinitroethylene and 1,1-Dibromodinitroethylene", Nguyen, N. V.; Baum, K., *Tetrahedron Letters*, in press.

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